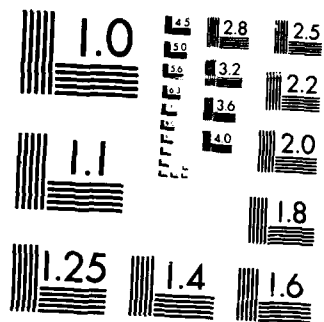


AD-A195 523

LOW TEMPERATURE PULSED PLASMA DEPOSITION PART 1 A NEW 1/1  
TECHNIQUE FOR THIN (II) SiC TECHNOLOGY LTD HARLOW  
(ENGLAND) SYSTEMS COMPONENTS DIV C A SCARSBROOK ET AL.  
12 APR 88 TA/583/1988/1444-P1-1 P/C 13/8 NL

UNCLASSIFIED

END  
DATE  
FILMED  
9 88



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

DTIC FILE COPY

①

2575G

AD-A195 523

OFFICE OF NAVAL RESEARCH

Contract N00014-87-G-0275

Task No. N62927

TECHNICAL REPORT NO. IR/503/1988/1444

LOW TEMPERATURE PULSED PLASMA DEPOSITION,  
PART 1 - A NEW TECHNIQUE FOR THIN FILM  
DEPOSITION WITH COMPLETE GAS DISSOCIATION

By

G A Scarsbrook, I P Llewellyn, S M Ojha, R A Heinecke

Presented at

European Vacuum Conference  
11-15 April 1988, Salford, England

and prepared for Publication in

Vacuum (Technology, Applications  
and Ion Physics)

STC Technology Ltd  
Systems Components Division  
London Road,  
Harlow, England, CM17 9NA

April 12th 1988

DTIC  
ELECTE  
MAY 16 1988  
S  
D  
E

Reproduction in whole or in part is permitted for any  
purpose of the United States Government.

This document has been approved for public release and sale:  
its distribution is unlimited.

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED/UNLIMITED		1b. RESTRICTIVE MARKINGS NONE	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT UNRESTRICTED	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) IR/503/1988/1444		5. MONITORING ORGANIZATION REPORT NUMBER(S) STL-No. 01	
6a. NAME OF PERFORMING ORGANIZATION STC TECHNOLOGY LTD	6b. OFFICE SYMBOL (If applicable) STL	7a. NAME OF MONITORING ORGANIZATION OFFICE OF NAVAL RESEARCH DR. R. W. SCHWARTZ	
6c. ADDRESS (City, State, and ZIP Code) LONDON ROAD HARLOW ESSEX. ENGLAND. CM17 9NA		7b. ADDRESS (City, State, and ZIP Code) CODE 38504 NAVAL WEAPONS CENTER CHINA LAKE, CA 93555-6001	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION OFFICE OF NAVAL RESEARCH	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-G-0275	
8c. ADDRESS (City, State, and ZIP Code) 800 N. QUINCY ST. ARLINGTON VA 22217-500 DR. R. POHANKA		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO. N62927	
11. TITLE (Include Security Classification) LOW TEMPERATURE PULSED PLASMA DEPOSITION: PART 1 A NEW TECHNIQUE FOR THIN FILM DEPOSITION WITH COMPLETE GAS DISSOCIATION			
12. PERSONAL AUTHOR(S) G.A. SCARBROOK, I.P. LLEWELLYN, S.M. OJHA, R.A. HEINECKE			
13a. TYPE OF REPORT TECHNICAL	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) 1988/APR/12	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) PULSED PLASMA; THIN FILM DEPOSITION; COMPLETE GAS DISSOCIATION; <i>RF</i>	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Conventional continuous plasma processes, for both deposition and etching, have three limitations. These limitations are: 1) incomplete gas dissociation, 2) gas depletion effects, and 3) substrate heating, either by the plasma itself or as a requirement of good film quality during deposition. However, all three of these disadvantages can be overcome in a novel process, developed by STL, where high power <i>RF</i> is pulsed. In this paper the pulsed plasma process and equipment is described in detail, and applications of its unique capabilities are discussed. <i>RF</i>			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED/UNLIMITED	
22a. NAME OF RESPONSIBLE INDIVIDUAL R. W. SCHWARTZ		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

# DISTRIBUTION LIST

Dr J C Pulver	Eastman Kodak Co, Hawkeye
Dr W Rhodes	GTE Laboratories, Waltham
Mr D Roy	Coors Porcelain Co, Golden
Dr J Savage	Royal Signals & Radar Establishment
Dr I G Talmy	Naval Surface Weapons Center
Mr W Tropsf	Applied Physics Lab, John Hopkins Univ.
Defense Documentation Center	
Dr R Pohanka	Office of Naval Research
Mr H Guard	Office of Naval Research
Mr R Jones	Office of Naval Research
Mr I Schafer	Naval Air Development Center
W Messick	Naval Surface Weapons Center
Dr N Tallan	Air Force Materials Laboratory
L Slotter	Naval Air Systems Command
Defense Metals & Ceramic Info	
Dr R W Schwartz	Naval Weapons Center
B Wilcox	Materials Sci Office
Metal & Ceramics Prg	Army Research Office
Chemistry Prog	Army Research Office
Code AX	Commandant of the Marine Corps
R N Katz	Army Mat & Mechan Research Center
Elec & Mats Sci Dir	Air Force Off of Sci Res/NE
Code 0712	Office of Naval Technology
Code 0725	Office of Naval Technology
Dr M Akinc	Iowa State University
Dr H E Bennett	Naval Weapons Center
Dr S Block	National Bureau of Standards
Dr J K Burdett	University of Chicago
Dr B Dunn	University of California
Dr G Gardopce	Perkin-Elmer Co, Danbury
Dr G Geoffrey	Pennsylvania State University
Dr A Harker	Rockwell Int'l Science Center
Dr D C Harris	Naval Weapons Center
Mr R A Heinecke	STC Technology Ltd
Dr L C Klein	Rutgers University
Dr P Melling	Battelle Columbus Laboratories
Dr R Messier	Pennsylvania State University
Dr G Messing	Pennsylvania State University
Dr P E D Morgan	Rockwell Int'l Sci Center
Dr C Pantano	Pennsylvania State University
Dr R Raj	Cornell University
Dr R Roy	Pennsylvania State University
Dr A Stacy	University of California, Berkeley
Dr R Tustison	Raytheon Company, Lexington
Dr W B White	Pennsylvania State University
Dr C Blackmon	Naval Surface Weapons Center
Dr J A Cox	Honeywell Systems & Res. Minneapolis
Dr P Klocek	Texas Instruments, Dallas
Dr D N Lewis	Naval Research Lab
Dr S Musikant	General Electric Co, Philadelphia
Dr D Perry	US Army Missile Cmd

2546G



## LOW TEMPERATURE PULSED PLASMA DEPOSITION

### PART 1 - A NEW TECHNIQUE FOR THIN FILM DEPOSITION WITH COMPLETE GAS DISSOCIATION

G Scarsbrook, I P Llewellyn, S M Ojha, R A Heinecke  
STC Technology Ltd, London Road, Harlow, Essex, England, CM17 9NA

Accession For	
NTIS	GRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced <input type="checkbox"/>	
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

#### ABSTRACT

Conventional continuous plasma processes, for both deposition and etching, have three limitations. These limitations are: 1) incomplete gas dissociation, 2) gas depletion effects, and 3) substrate heating, either by the plasma itself or as a requirement of good film quality during deposition. However, all three of these disadvantages can be overcome in a novel process where high power RF is pulsed. In this paper the pulsed plasma process and equipment is described in detail, and applications of its unique capabilities are discussed.

#### INTRODUCTION

Thin films deposited using plasma processing are vital for many of the current electronic devices, and are important elements in many optical protective, and decorative applications (for a review see <sup>1</sup>). Consequently,

conventional plasma processing is a major field of research and development, focussing particularly on increasing deposition rates, improving film quality and uniformity, and developing the process to allow deposition onto a wider range of substrates than can presently be used. Development of these aspects is largely controlled by three related limitations of the continuous plasma process, namely incomplete gas dissociation, gas depletion, and the need for substrate heating. Incomplete gas dissociation stems from the low discharge power that is conventionally used in the deposition process, which in turn requires further applied substrate heating to activate the additional surface reactions necessary to produce good films from the poorly dissociated gases. Gas depletion effects, causing non-uniformity across the substrate, are usually controlled by utilising only a small fraction of the available reactants. Not only is this wasteful, limiting the method to reactants that are comparatively inexpensive, but also the high concentration of reactive reagents in the rotary pump exhaust can lead to a serious safety hazard.

These limitations can be overcome in a patented <sup>2</sup> plasma process described here, whose key feature is high power radio-frequency (RF) pulses, to ensure complete dissociation of the reagent gases, coupled with a very low duty cycle resulting in a low average power. As complete gas exchange can be allowed to occur between RF pulses, and gas flow on the timescale of the RF pulses used (typically 200  $\mu$ s) is negligible, depletion effects do not occur. An additional facility is that the gas composition for each RF pulse can be individually selected, giving better control on the composition of the deposited film, and also enabling the rapid production of multilayer films.

Firstly, an overview of the process and equipment is given and experimental evidence of gas dissociation behaviour presented, and then typical deposition conditions, for example films, are described. Finally, general and specific applications of this technique for producing unique films and structures are discussed.

#### PROCESS OVERVIEW

Pulsed plasma deposition can be implemented in the same two ways as conventional plasma deposition, namely using an inductive (or barrel type) discharge or a capacitive (or parallel plate) discharge. The two methods are distinguished by the method by which the RF power is coupled to the discharge; in the inductive reactor the discharge is sustained by the high alternating magnetic fields generated using a coil wrapped around the chamber, whereas in the capacitive reactor the discharge is sustained by the high voltages between two RF electrodes within the chamber. Both methods are used in this study and will be described separately.

#### FIGURE 1 HERE

The capacitive reactor chamber, shown in Figure 1, consists of a six-way, 150 mm stainless steel cross, with gas flow from right to left, electrode entry top and bottom, viewing window at the front, and a port at the rear used to attach diagnostic equipment such as a visible/U.V. spectrometer or a mass spectrometer. Gas pumping is achieved by a roots/rotary combination pump stack with a nominal pumping speed of  $250 \text{ m}^3/\text{h}$ . Typical operating pressures are 50 to 300 mTorr as measured by a capacitive pressure gauge



connected directly to the chamber. The pumping speed at the chamber can be controlled by a butterfly throttle valve, which allows control of the reactor pressure independently of the gas flow rates.

The reactor, gas input lines and pumping pipework are designed to allow maximum conductance and consequently minimum pressure drop across the reactor. Each of the eight gas entry lines feeds onto a common manifold and consists of a shut-off valve (SVn), a mass flow controller (MFCn), a specific gas volume (VOLn), and a rapid operation pulsing valve (PVn). During deposition with a constant gas composition for each RF pulse, both the shut off valve and the pulsing valve can be left open, and continuous gas flow controlled by the mass flow controller. During pulsed gas deposition the shut-off valve is again left open, and the mass flow controller passes a constant gas flow, but the pulsing valve is rapidly opened and closed in sequence with the RF pulsing. The gas which flows through the mass flow controller whilst the pulsing valve is closed pressurises the gas volume immediately prior to the pulsing valve until the valve is opened again. In this mode of operation it is important to generate the RF pulse at the correct time after the pulsing valve is opened, that is after the gas has reached the chamber and complete gas exchange has occurred, but before the gas has been pumped away. The sequencing of the gases and the discharge pulse is controlled by a microcomputer, which is capable of controlling all operations at greater than 100 RF pulses per second, each potentially with a different gas composition. Practical constraints of gas pumping/exchange rates and pulsing valve operation times currently limit processing to about 60 RF pulses per second.

Reactor electrode design is critical, since very high power pulsed RF can result in arcing within the reactor if the electrode design is poor. Electrodes are typically made of stainless steel or copper, consisting of hollow discs about 110 mm in diameter and 40 mm thick mounted on a 12.7 mm diameter stem through which cooling water is entered and extracted. The ground electrode is not normally insulated, but mounted by its stem through a compression fitting in the flange on one arm of the reactor cross. The RF electrode is similar, except that a conformal PTFE insulator, about 8 mm thick, covers all the electrode (and stem) except for the top surface and about 5 mm down the side. Compression fittings are used to seal the electrode to the insulator at the end of the stem, and to mount the whole assembly into a flange. The advantage of copper over the stainless steel as an electrode material is that, whilst the latter is more chemically stable in a plasma, the high thermal conductivity and low thermal electron emission of copper together make it much less prone to spurious arcing. The apparatus can be run in both plasma mode (sample on ground electrode) and in ion bombardment mode (sample on RF electrode) by switching over the two electrodes in the top and bottom arms of the cross.

FIGURE 2 HERE

An alternative form of the deposition chamber and electrodes is used for inductively coupled discharges (Figure 2). Inductively coupling the discharge avoids the effects of ion or electron bombardment which result on the RF and grounded electrode respectively of a capacitively coupled system due to the large DC bias generated at the RF electrode. In this arrangement the reactor used is a quartz tube of about 100 mm diameter surrounded by an

induction coil consisting of 20 mm wide copper plate wrapped around the tube twice over a length of about 300 mm. As the discharge volume is higher in this configuration than for the parallel plate, it is found necessary to operate this plant at a lower pressure (20 to 100 mTorr) in order to achieve complete dissociation, and in order to do this a 12 inch oil diffusion pump backed by a 40 m<sup>3</sup>/h rotary pump is used. Gas entry to the tube is at the rear and consists of a manifold connected to four mass flow controllers. As the pumping speed and the conduction of the pipes is lower in this configuration, no effort has been made to pulse the gas flow. The substrates are placed into the reactor via a door at one end of the tube which also contains a window to allow the discharge to be viewed. In operation it has been found that the discharge is most intense near the walls of the reactor and that the power density at the centre of the tube is not sufficient to achieve good quality films. Substrates are therefore placed as close to the reactor wall as possible, and to facilitate this for flat substrates a variety of the tube shapes have been used, including both square and rectangular sections of similar cross-sectional area to the round tube previously described. A capacitance pressure gauge, mass spectrometer, and optical spectrometer are attached to the reactor in order to provide diagnostic information about the plasma.

For both configurations the discharge power was supplied by a 50 kW, 13.56 MHz radio frequency generator (Plasma Therm) which has been specifically adapted so that it can be pulsed by varying the voltage on the grid on the pre-amplifier RF valve. Pulse rise time is limited by the capacitance of the grid of the RF power amplifier tube to about 20  $\mu$ s. Forward and reflected power are measured in the 50 ohm coaxial line leading to the matching box,

using a standard industrial directional coupler and displayed on a digital storage scope. The rise time of the forward power signal into a 50 ohm dummy load is about 30  $\mu$ s. The matching box is a standard "L" configuration using high voltage (20 kV) matching capacitors and one of a series of fixed value coils, which together allow the full range of operating pressures to be adequately covered. As the instantaneous field strength produced in the equipment is very high, great care has to be taken in enclosing all RF parts in suitable metal shielding to prevent possibly hazardous exposure to the RF field.

#### Verification of Gas Dissociation Behaviour

The pulsed plasma technique relies on the high degree of dissociation of the reactant gases when sufficient power is present in the RF pulse. The energy density required to break all bonds of gas molecules present between the electrodes can be simply calculated given the operating pressure and the relevant bond dissociation energies. For example, depositing silicon nitride using a partial pressure of  $\text{SiH}_4$  of 10 mTorr and  $\text{N}_2$  of 100 mTorr in the capacitive reactor requires a pulse energy of at least 5 J to completely dissociate the reagents to ground state atoms. In practice the process is unlikely to be 100% efficient and a method is required to determine the minimum energy required to achieve complete dissociation.

The most obvious way to do this is to examine the quality of the films as the power input to the plasma is varied: for silicon nitride the easiest methods are to use infra-red absorption to measure the amount of hydrogen bonded in the film, and to measure the buffered HF (BHF) etch rate as

a measure of the overall film density. The former is a good measure of dissociation in the gas phase since any partially dissociated silane radicals arriving at the film are readily incorporated<sup>4, 8</sup> and the latter is an accepted method for categorising silicon nitride quality<sup>5</sup>. In order to obtain the infra-red spectrum of the deposited material, films were deposited onto caesium bromide plates and the spectra was taken using Fourier transform infra-red spectrometry. The BHF etch rate was found by depositing films on silicon and masking of an area of the film with photoresist before etching the sample in a BHF for a known time. The photoresist was then removed and the step formed was measured using a surface-profiling technique. Both these methods were used to examine the film quality of the silicon nitride films as the pulse power was varied. The results show that low BHF etch rates and the least amount of bonded hydrogen in the film occur when the pulse input energy was about twice that required to fully dissociate the molecules. Figure 3 shows the effect on the Si-H stretching mode in the infra-red spectra of the silicon nitride films in the capacitive reactor as the pulse energy is reduced from 50 kW to 10 kW. This clearly shows a marked difference in bonded hydrogen between the two power levels. Figure 4 shows the variation of BHF rate, deposition rate, and refractive index of the silicon nitride film as the pulse energy is varied. It is apparent that a pulse energy of at least 8 J is required to produce high quality films, and below this energy the properties of the film deteriorate rapidly.

FIGURE 3 HERE

FIGURE 4 HERE

A more direct method of analysing the discharge is to monitor the light from the discharge using a spectrometer. Since the spectra of many of the species present are well known<sup>3</sup>, the spectra of the discharge as the power level is varied can directly monitor the creation and destruction of species in the plasma. Figure 5 shows the variation of the integrated light intensity of atomic lines of nitrogen, silicon, and carbon atoms from discharges of nitrogen, silane, and methane, respectively at a pressure of 0.1 torr in the inductive reactor using a 300  $\mu$ s pulse width. It can be seen that the signal peaks at a power level, and further increases in power do not lead to an increase in output intensity. If one can equate the output intensity with the concentration of the ground state species present in the plasma, one can therefore conclude that the atomic concentration of the atom concerned has reached a maximum at this power level. An attempt was also made to monitor the creation and destruction of these atoms in the plasma pulse by displaying the output from the photomultiplier tube on a digital oscilloscope. Figure 6 shows curves obtained using discharges of silane and nitrogen in the inductive reactor at 0.1 torr. It can be seen that the silicon atoms are formed very quickly at the start of the pulse but then decay rapidly due to diffusion to the walls and consequent removal. The nitrogen atoms take much longer to form and generally do not reach a maximum concentration until 150  $\mu$ s into the pulse, even at full discharge power. These results suggested that the high bond strength of nitrogen was slowing down the dissociation into atoms and that short pulse widths (i.e. < 150  $\mu$ s) would deposit silicon rich films. When films were deposited under such conditions they were indeed found to be brown, confirming the spectroscopic study. Clearly, time-resolved spectroscopic evaluation of the plasma can not only characterise the process but also provide mechanistic details on how the

deposition occurs. Work is continuing to quantify these results further in order to allow the scaling up of the process to industrial scale.

FIGURE 5 HERE

FIGURE 6 HERE

#### Typical Deposition Conditions

The deposition of two specific materials will be discussed here, namely  $\text{SiN}_x$  and  $\text{SiO}_x$ . Both of these films have  $\text{SiH}_4$  as the source of Si, and  $\text{N}_2$  and  $\text{CO}_2$  respectively as the source of the co-atom. Unless otherwise stated, the films discussed in this section were deposited in the capacitive reactor mode. Films deposited using the inductive reactor are very similar, with the exception that they exhibit stress cracking on temperature cycling. This is thought to be the result of the low ion bombardment in this mode of operation and agrees with the observation of other workers (see for example<sup>1</sup>).

Typical deposition conditions for SiN are to use a 200  $\mu\text{s}$ , 50 kW RF pulse and a pulse rate of 30 Hz, at a chamber pressure of 250 mTorr. The flow of silane is typically 100 sccm and the flow of nitrogen typically 1000 sccm; the majority of the nitrogen being there to bring the pressure up to suitable level to sustain the discharge. Under such conditions the self-induced bias voltage on the RF electrode is about 3000 V. Samples placed on this electrode suffer sustained ion bombardment whereas those on the counter (grounded) electrode suffer high electron bombardment. The film quality consequently varies quite significantly between the two electrodes; the ion bombarded

sample feeling harder on a simple 'tweezer' scratch test and suffering much less from stress cracking than the electron bombarded film. The electron bombarded films also appear to get hotter than the ion bombarded sample and this can be significant when considering adhesion to thermally sensitive substrates (e.g. plastics). Standard data on the deposited film using this method is shown in Table 1. For comparison, conventional plasma-deposited film deposited at a much higher substrate temperature (650 K) are reported<sup>6, 8</sup> to give a BHF etch rate of 200 Å/min and a refractive index of 2.0. It therefore seems that the pulsed plasma film deposited at room temperature is comparable in quality to the conventional plasma film deposited at temperatures in excess of 600 K. Further work is planned to compare the properties of this film against the properties of thermally grown, chemical vapour deposited material grown at temperatures above 1000 K.

TABLE 1 HERE

It is possible to deposit silicon oxide films using the same conditions as used for silicon nitride, but with the nitrogen replaced by carbon dioxide. Films deposited under these conditions are light brown in colour and Auger analysis of the film composition reveals the inclusion of up to 10% atomic carbon, which comes from the dissociated carbon dioxide at these high power levels. Colourless and stoichiometric silicon dioxide can be formed using carbon dioxide by discharging carbon dioxide alone in a second pulse after discharging the depositing silane/carbon dioxide pulse; the second pulse reoxidises up the deposited carbon to carbon monoxide. Films deposited in this manner have the properties given in Table 2 and appear to be similar to silicon dioxide films deposited by other means<sup>7</sup> or indeed similar to the bulk material.



## TABLE 2 HERE

Areas of Application

This new deposition technique has a large number of potential application areas in a wide number of fields. Currently under evaluation is the use of the process to produce protective films on plastics, to produce optical coatings on temperature sensitive materials and its use as a low temperature moisture barrier layer on integrated circuits. Future publications will describe the ability of the process to produce thin layer 'sandwich' structures and the consequent applications of the technique to high performance optoelectronic devices; also the use of the process for the preparation of novel material systems for infrared window applications.

Conclusions

A major new low pressure plasma deposition technique has been described, which allows the deposition of bulk quality films at or about room temperature. The method is differentiated from other plasma techniques by the use of a high power pulsed discharge to cause a high degree of dissociation to be present in the gas phase. This in turn allows rapid characterisation of the deposition by the use of time resolved spectroscopy of the discharge glow. Although only two materials (silicon oxide and silicon nitride) have been described here, the method has already been demonstrated for a wide variety of materials, including metals and semiconductors at high deposition rates at room temperature. Future publications will concentrate on individual materials and structures in greater detail and will demonstrate the versatility of the technique.

Acknowledgements

The authors acknowledge financial support for the work from ITT in the early stages, and latterly from STC Technology Ltd, US Naval Weapons Center, and US SDI/IST through the Office of Naval Research. They also acknowledge the assistance given by STL Site Services and Mechanical Engineering Services Departments in the construction of equipment, and the STL Materials Evaluation Centre for help with the evaluation of the films.

Property	Measured by	Result
Composition	Auger Analysis	$\text{Si}_3\text{N}_4$
Colour	Visual Inspection	Colourless even for Thicknesses $> 10 \mu\text{m}$
Microstructure	SEM examination	Featureless (resolution $< 250 \text{ \AA}$ )
Refractive index	Ellipsometry	2.0 at 633 nm
Buffer HF etch rate	Standard test as described in[6]	$< 100 \text{ \AA}/\text{min}$
Temperature stability	Baking for 48 hours at 473 K	Stable with no sign of stress cracking
Infra-red absorption spectrum	Fourier Transform Spectroscopy	Similar to plasma deposited material deposited at $> 400^\circ\text{C}$
Deposition rate	Surface profiling over step	$3000 \text{ \AA}/\text{min}$ typical

Table 1: Properties of pulsed plasma deposited silicon nitride. The deposition conditions were as follows: pulse width 250  $\mu\text{s}$  with 50 kW power input, partial pressure  $\text{SiH}_4$  25 mTorr, partial pressure  $\text{N}_2$  250 mTorr.

Property	Measured by	Result
Composition	Auger Analysis	$\text{SiO}_{2.09}$
Colour	Visual Inspection	Colourless, even for films 10 micron thick
Microstructure	SEM examination	Featureless (resolution $< 250 \text{ \AA}$ )
Refractive index	Ellipsometry	1.48 at 633 nm
Visible Transparency	Visible spectroscopy	$> 99.9\%$ at 500 nm for a $1 \mu\text{m}$ thickness
Temperature Stability	Baking for 48 hours at 473 K	No change in appearance and no stress cracking observed
Bond strength to plastics (polycarbonate)	Stud pull tests	$> 40\,000 \text{ Nm}^{-2}$
Deposition rate	Surface profiling over step	$3000 \text{ \AA}/\text{min}$ typical

Table 2: Properties of pulsed plasma deposited silicon dioxide. The deposition conditions are as follows: First pulse (50 kW discharge power, 150  $\mu\text{s}$ ) of 25 mTorr of  $\text{SiH}_4$ , 250 mTorr of  $\text{CO}_2$ . Second pulse (50 kW discharge power, 150  $\mu\text{s}$ ) of 250 mTorr of  $\text{CO}_2$  only.

## REFERENCES

- 1 Hass, M, Francombe, J Vossen "Physics of Thin Films" Vol. 12 Academic Press London (1982).
- 2 R A Heinecke, S M Ojha, M J Cooke UK Patent GB 2 105 729B "Surface Processing of a Substrate Material".
- 3 R W Pearse, A G Gaydon, "The Identification of Molecular Spectra" Chapman & Hall Ltd., London (1965).
- 4 S Futija, N Zhou, H Toyoshima, T Ohishi, A Sasaki, Int. Electron Devices Mtg. Tech. Digest., San Francisco, 28.3, 630-3 (1984).
- 5 T Goto, T Hirai J, Mat. Science 18, 3387-3392 (1983)
- 6 W A Lanford, M J Rand, J. Appl. Phys. 49(4), (1978).
- 7 A C Adams, Solid State Tech. 26(4), 135-139 1983
- 8 H Dun, P Pan, F R White, R W Douse, J. Electrochem. Soc.: Solid State Science and Technology 128(7), 1555-1563 (1981).

List of Figures

Fig. 1. Pulsed plasma capacitive reactor

Fig. 2. Pulsed plasma inductive reactor

Fig. 3. Part of the Fourier transform infrared spectra of silicon nitride showing Si-H peak at  $2150\text{ cm}^{-1}$ . Upper curve: silicon nitride deposited using 10 kW pulse power. Lower curve: silicon nitride deposited using 50 kW pulse power. The slope of the base line is due to scatter in the caesium bromide substrate.

Fig. 4. Effect of pulse power on silicon nitride film properties. Films deposited in capacitive reactor at 250 mTorr, 250  $\mu\text{s}$  pulse width.

Fig. 5. Variation of spectroscopic output intensities  $I^*$  with power.

Fig. 6. Time resolved plasma power is shown on the upper trace. The lower trace shows (i)  $\text{Si}^*$  emission intensity, and (ii)  $\text{N}^*$  emission intensity. Pulse width 250  $\mu\text{s}$

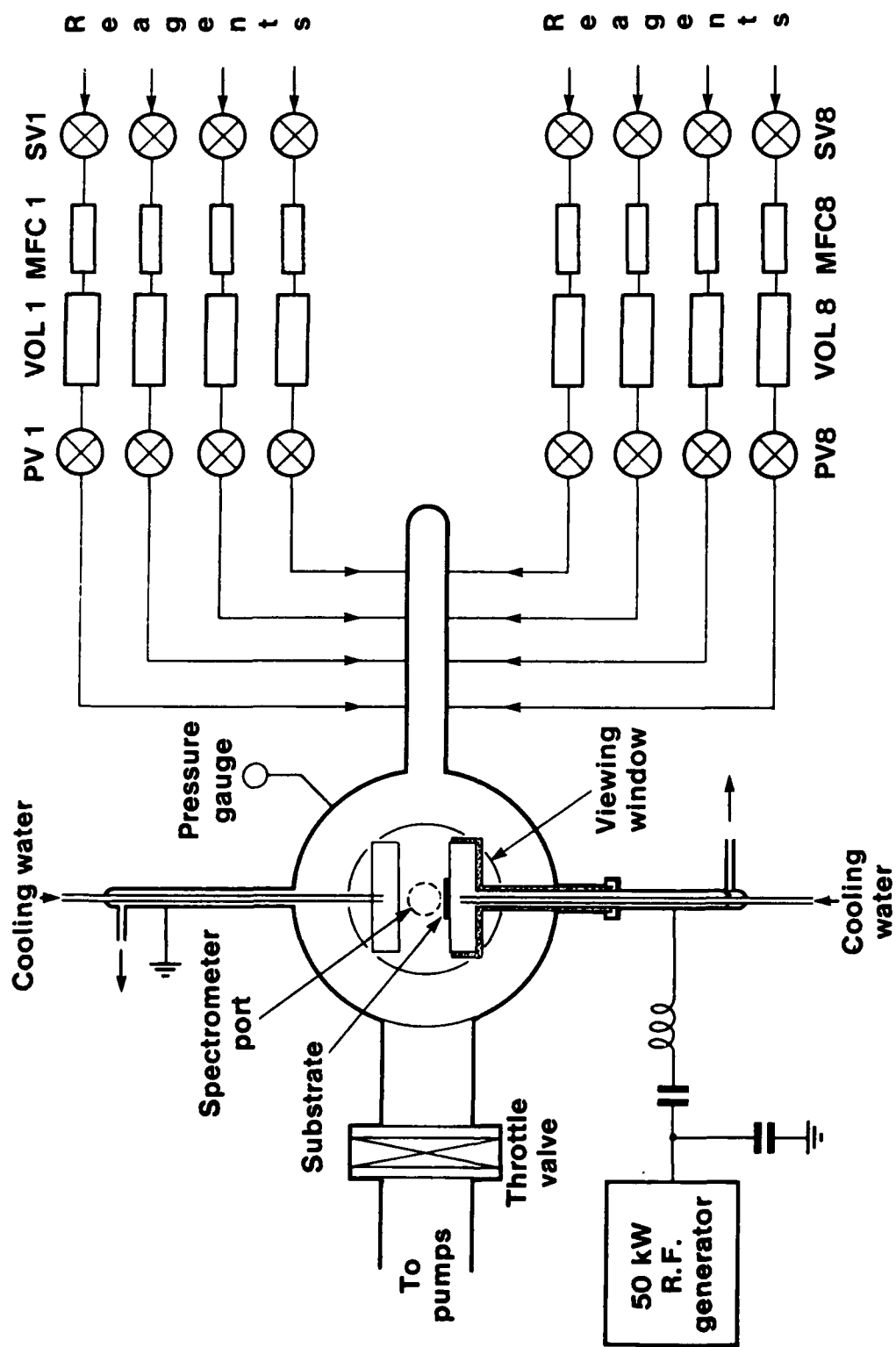


Fig. 1 Pulsed plasma capacitive reactor

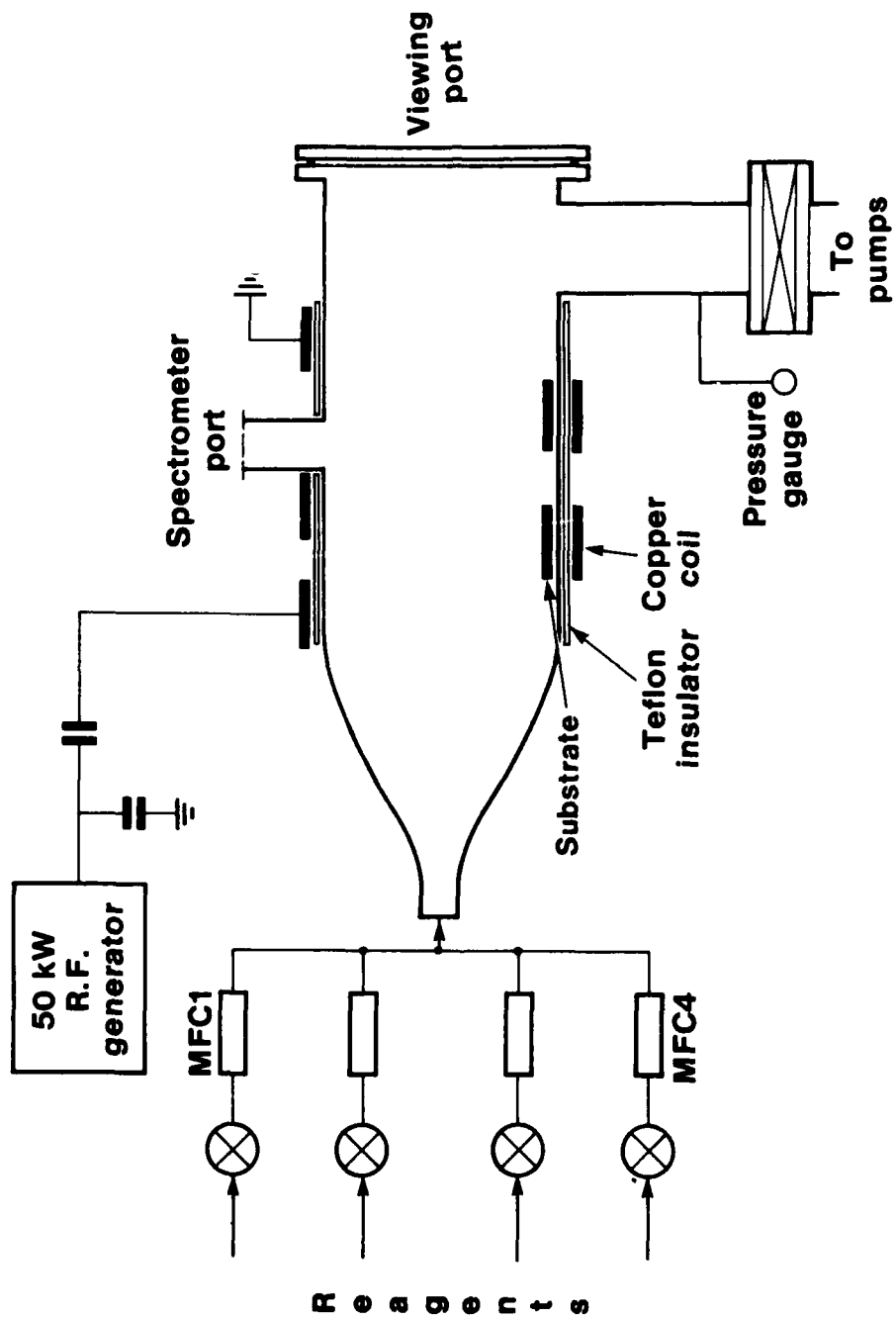
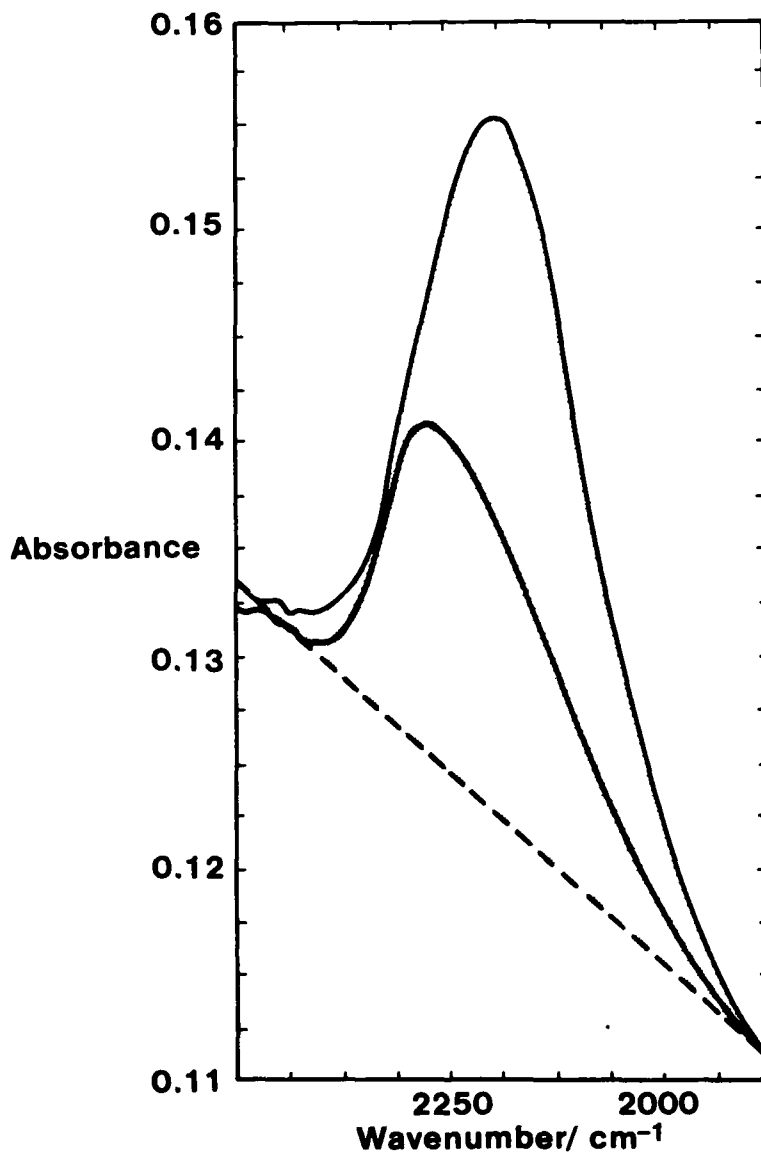
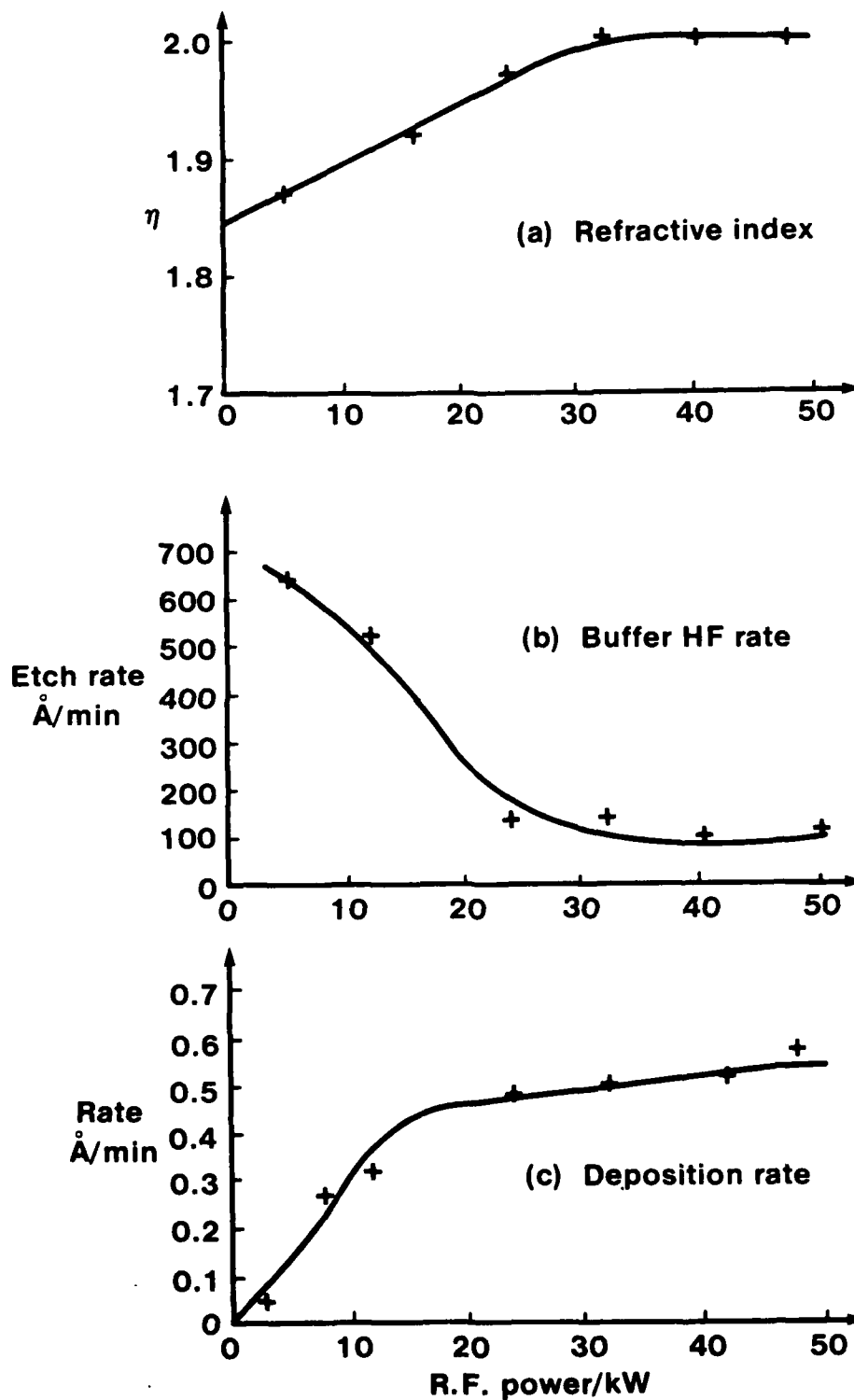


Fig. 2 pulsed plasma inductive reactor



**Fig. 3 Part of the Fourier transform infrared spectra of silicon nitride showing Si-H peak at 2150cm<sup>-1</sup>. Upper curve: silicon nitride deposited using 10kW pulse power. Lower curve: silicon nitride deposited using 50kW pulse power. The slope of the base line is due to scatter in the caesium bromide substrate.**





**Fig. 4 Effect of pulse power on silicon nitride film properties. Films deposited in capacitive reactor at 250m Torr, 250 $\mu$ s pulse width**

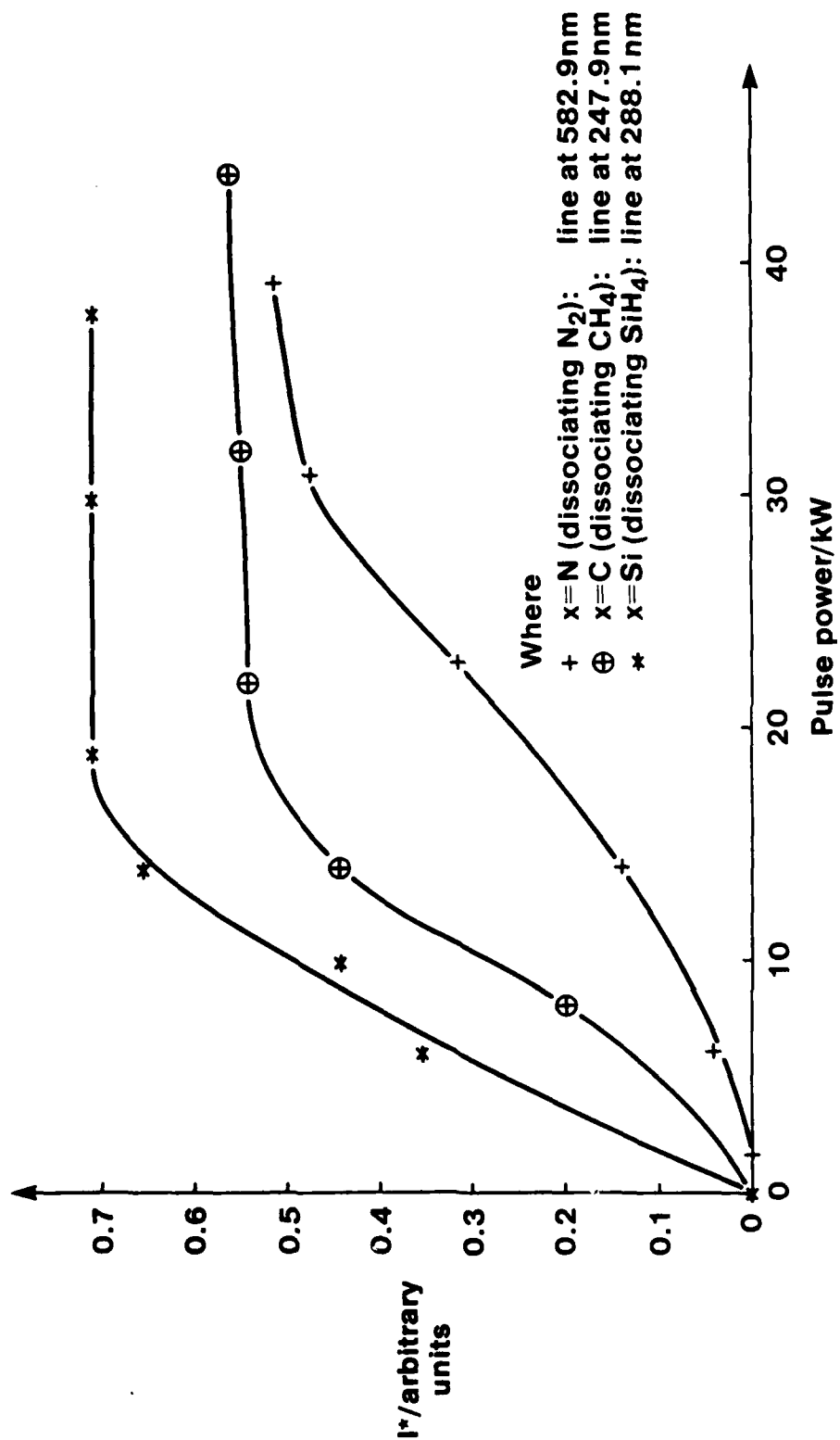
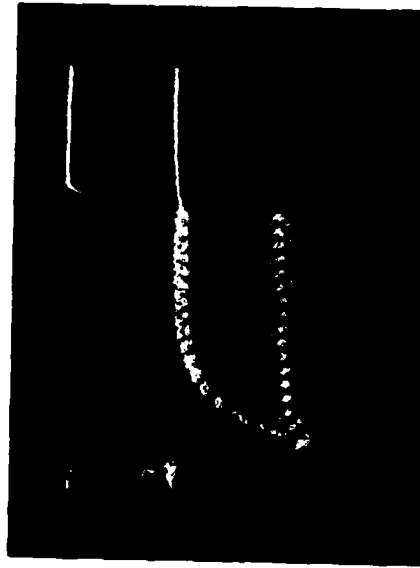


Fig. 5 Variation of spectroscopic output intensities I\* with power

(i)



(ii)

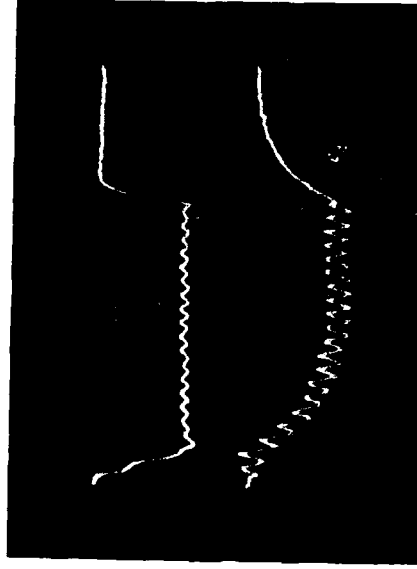


Fig. 6 Time resolved plasma power is shown on the upper trace. The lower trace shows (i) Si<sup>+</sup> emission intensity, and (ii) N<sup>+</sup> emission intensity. Pulse width 250  $\mu$ s.

DATE  
FILMED  
- 8